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FINELY DISPERSE HEAT-RESISTANT REFRACTORIES BASED ON TECHNOGENIC MATERIALS

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Investigation results of application of carborundum plate scrap in the production of finely disperse heat-resistant saggers by the slip casting method are presented. The main physicochemical properties of the considered mixtures based on plate scrap are not inferior to those of mixtures based on silicon carbide. Experimental lots of saggers of different shapes exhibited good service properties. At the same time, the production cost of saggers is reduced to approximately one-third.

The purpose of refractories is to protect articles in firing from the direct effect of the furnace gas and abrupt temperature fluctuations, impede contamination and mechanical damage of the surface of the articles, prevent the articles from adhesion, and contribute to the product having a homogeneous temperature.

Strict requirements are placed on refractories intended for accelerated firing, with respect to their heat resistance, thermal conduction, heat capacity, compression and bending strength, and mean density.

Silicon carbide refractories satisfy these requirements best [1, 2]. Effective methods for increasing heat resistance of refractories are as follows: increase in ultimate strength due to correct selection of the granular composition, the molding method, and the optimum firing temperature; increase in thermal conductivity due to introduction of silicon carbide; decrease in elasticity modulus due to addition of technical alumina to silicon carbide mixtures; decrease in the TCLE of mixtures through introduction of additives facilitating the formation of compounds with a low TCLE (mullite etc.) under firing.

For accelerated firing, the strength of refractories has to be increased, since in this case the refractories should have a minimum thickness and weight. The thickness of a refractory with high heat resistance should not exceed more than 2 – 3 times the thickness of the fired article [1].

Deterioration of the service conditions of refractories arising from the intensified firing process predetermines the selection of the main materials to be used as refractories in the immediate future: cordierite, mullite, silicon carbide, and, to a lesser extent, clay chamotte, although the latter type of refractories is still widely used in industry [1, 2].

The best physicomechanical parameters and longevity are exhibited by saggers and refractories made of mixtures containing silicon carbide [2, 3].

Silicon carbide mixtures have an increased (up to 48 – 99%) content of SiC.

Saggers and refractories are mostly made of carborundum whose granulation numbers correspond to three fractions (mm): 2.0 – 1.0 (No. 160 – 100), 0.8 – 0.5 (No. 65 – 50), and 0.16 – 0.08 (No. 12 – 8), which are taken in the ratio 1 : (1.0 – 1.2) : (1.8 – 2.0). With such composition, the fine fractions of SiC fill the spaces between large grains, which contributes to increased strength of the refractories [4].

Carborundum mixtures have low shrinkage, increased mechanical strength, resistance to deformation at high temperatures, and thermal resistance determined by a low TCLE and high thermal conductivity.

Porcelain factories widely use a refractory based on silicon carbide with a clay binder, in which the SiC content is up to 95%. The refractory made of this mixture has the following basic parameters: average density 2.4 g/cm^3, TCLE $5.5 \times 10^{-6}\,K^{-1}$, service temperature 1400°C, bending strength 10 MPa [1].

For a long time the Gzhel' Company in firing porcelain articles used a clay chamotte sagger whose service life did not exceed 2 – 3 cycles.

Recently, research was carried out to develop a technology for making silicon carbide saggers based on a clay binder using slip casting in gypsum molds [5].

The content of silicon carbide in the mixtures varied from 30 to 55%, and the slip moisture was 35 – 36%. After a second firing, the bending strength attained 17 – 44 MPa. The overall shrinkage was within the limit of 4.0 – 5.5%. The service life of the saggers was at least 50 cycles. Thus, the development of heat-resistant saggers containing silicon

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carbide and made by slip casting is a promising line for further improvement of refractories produced at the Gzhel' company.

Implementation of the technology of sagger manufacturing by slip casting makes it possible to produce durable saggers of virtually any size, which is essential in the production of short-run or unique pieces.

However, owing to the high cost of silicon carbide (6000 – 7000 rubles per ton), wide application of the technology of finely disperse refractories at porcelain factories is limited.

Factories in the Gzhel'skii district which use silicon carbide plates for stack cars accumulate a lot of broken plates and saggers which either are not recycled at all, or are partly added to chamotte sagger mixtures.

The Gzhel' company carried out research in using broken carborundum plates for sagger production using the slip casting method.

The application of technogenic materials in manufacturing heat-resistant refractories allows for utilization of plate and sagger scrap and significantly reduces the production cost of refractories by replacing expensive silicon carbide material.

The purpose of the present study is to establish the possibility of using carborundum plate and sagger waste in manufacturing heat-resistant saggers.

The optimum composition taken as the reference mixture (KK) in the study was based on SiC polished powder that had been produced earlier [5] and contained 55% silicon carbide, 30% argillaceous components, and 10% alumina.

The present study contemplates the following mixture compositions based on carborundum plate waste:

sagger mixture M1 contained 40% carborundum plate scrap, mixture M2 — 50%, and mixture M3 — 60%;

content of argillaceous materials (refractory clay + kaolin) in the mixtures: M1 — 40%, M2 — 35%, M3 — 30%;

content of technical alumina in the mixtures: M1 — 20%, M2 — 15%, M3 — 10%.

Electrolytes were introduced in the mixtures above 100%: liquid glass 0.6%, soda ash 0.2%, sodium pyrophosphate 0.15% of dry material weight.

The chemical composition of carborundum plate scrap (wt.%) is 23.16 SiO_2, 1.69 Al_2O_3, 0.36 CaO, 0.26 MgO, 0.17 K_2O, 0.19 Na_2O, traces of FeO_3, TiO_2, and SO_3.

The chemical composition of the plate waste testifies to a sufficiently high content of SiC, since in multiple firing only the SiC grains contained in the surface layer to a depth of 10 – 12 μm participate in chemical reactions.

Fine grinding of the mixture components was carried out in a ball mill by joint milling to a residue of 8 – 10% on a sieve No. 0063. The slip moisture was kept constant at 32%. The rheological characteristics of the slip are given in Table 1.

It can be seen that with increasing amount of waste introduced in the mixture, the slip density grows from 1.76 to 1.89 g/cm^3, but is slightly lower than that of the reference mixture KK based on silicon carbide. This is due to the fact that mixtures based on the plate scrap have a higher overall content of argillaceous materials, which are introduced in the course of manufacturing silicon carbide plates and saggers. According to the data of the Dulevskii Porcelain Factory, the clay content in the sagger mixture based on SiC is 30%.

The physicomechanical properties of samples of the tested mixtures are shown in Table 2.

The samples based on carborundum plate waste are not inferior to the initial samples in their main parameters. As the content of carborundum plate scrap in the mixtures increases from 40 to 60%, the bending strength increases from 40 to 53 MPa, the water absorption increases from 15.5 to 17.7%, the total shrinkage decreases from 5.8 to 3.8 %, the volume weight increases from 1.74 to 1.78 g/cm^3, and the thermal resistance of samples after 10 thermal cycles exhibits an increase in the bending strength from 33 to 41 MPa. The TCLE virtually does not change, but its values in all cases are higher than that of the initial mixture (Fig. 1).

The increase in the TCLE in the temperature interval of 180 – 270°C in the mixtures based on plate scrap is due to

TABLE 1

Slip parameters	Mixture			
	KK	M1	M2	M3
Density, g/cm^3	1.91	1.76	1.77	1.79
Fluidity, sec	4	6	5	4
Thickening coefficient	2.47	1.80	1.60	1.25

TABLE 2

Parameter	Mixture			
	KK	M1	M2	M3
Static bending strength, MPa	40.0	40.4	49.0	53.0
Water absorption, %	18.0	15.5	16.4	17.7
Overall shrinkage, %	5.3	5.8	5.1	3.8
Porosity, %	20.0	18.8	21.0	19.5
TCLE in the temperature interval 50 – 600°C, 10^{-6} K^{-1}	4.58 – 5.00	6.10 – 7.20	6.20 – 7.40	6.30 – 7.70
Volume weight, g/cm^3	1.80	1.74	1.76	1.78
Heat resistance of samples after 10 thermal cycles (R_{fab}), MPa	38.0	32.0	36.9	41.1

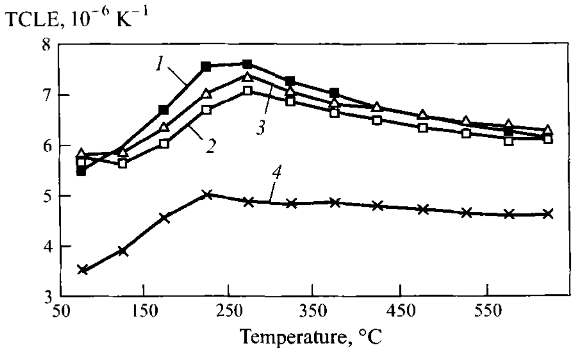

Fig. 1. Variation in TCLE in mixtures M1 (*1*), M2 (*2*) M3 (*3*), and KK (*4*).

the fact that β-cristobalite in this temperature interval soon converts to α-cristobalite, which is accompanied by changes in the volume of mixtures M1, M2, and M3.

A study of the microstructure of finely disperse refractories based on plate scrap fired at temperature 1350°C revealed a more perceptible degree of mullitization compared to the reference mixture KK and a higher content of the vitreous phase. An edge around SiC grains is clearly visible.

The content of SiC grains in the mixtures (%) is M1 – 38.0, M2 – 37.5, M3 – 36.2; the average size of SiC grains (μm) is M1 28.7, M2 26.7, M3 23.4. The shape of SiC grains is fragmentary and elongated. The porosity in the mixtures is (%) is M1 18.8, M2 21.0, M3 19.5; the average pore size (μm) is M1 – 16.7, M2 – 16.1, M3 – 13.7. The pore shape is mostly irregular, some are fused by 2 – 3 pores, and the pores are isometric.

The mixture contains quartz grains from 10 – 15 to 40 μm (maximum size 80 – 100 μm) and alumina grains from 10 – 15 to 50 – 60 μm.

TABLE 3

Cost items	Prescribed expense rate, %	Production cost (rubles) of sagger based on	
		silicon carbide	silicon carbide plate scrap
Production cost of 1 ton of slip for silicon carbide sagger			
Materials	–	3466.8	356.6
Fuel and electricity	–	2.702	2.702
Wages:			
basic wage	–	6.042	6.042
supplementary wage	17	1.027	1.027
Social insurance allocations	38.5	2.8	2.8
Company overhead expenses	145	8.8	8.8
TOTAL	–	3488.1	377.9
Production cost of a silicon carbide sagger			
Materials	–	58.5	6.1
Fuel and electricity	–	2.702	2.702
Wages:			
basic wage	–	6.042	6.042
supplementary wage	18.8	1.136	1.136
Social insurance allocations	39.5	2.8	2.8
Company overhead expenses	145	8.8	8.8
TOTAL production cost	–	79.97	27.56

The glass ceramic mixture contains mullite clusters; the size of mullite needles ranges from 2 – 5 to 7 – 10 μm.

All mixtures have inhomogeneous structure.

The silicon carbide content in a finished product made of the initial mixture KK was around 31%, the maximum grain size in this case attained 120 – 150 μm, and the average size was 34.6 μm. The silicon carbide grains have an edge about 2 μm wide.

Quartz grains are present in insignificant quantities (0.5%), with a maximum size of 100 – 120 μm. They also have an edge about 2 μm wide, which corresponds to their fusing.

The pore shape is elongated and irregular, and the maximum length is 80 – 100 μm, with an average size of 14.5 μm. The pore content is 20%. The vitreous phase is represented by glass with uniform fine crystallization.

The scrap of carborundum plates is a previously sintered material in which chemical reactions have been completed. It contains residual quartz which has undergone modifying transformations, mullite, a vitreous phase, and SiC grains that have not reacted. Therefore, the formation of the microstructure and the skeleton of the refractory in the considered mixtures proceeds more completely than in the reference mixture.

Based on the performed study and analysis of the obtained data, the optimum composition for the sagger mixture was selected, namely, M3 mixture that contains 60% plate scrap.

Industrial testing of M3 mixture at the Gzhel' company validated the possibility of using carborundum plate scrap in sagger mixtures. The testing was carried out following the standard technology of manufacturing silicon carbide saggers accepted in the company.

Experimental lots of saggers were made of M3 mixture with wall thickness 5 – 8 mm: round saggers 270 mm in diameter and 80 mm high (10 pieces); ellipsoid saggers with a major axis of 410 mm and a minor axis of 260 mm, and 55 mm high (40 pieces); round saggers 360 mm in diameter and 60 mm high (20 pieces); saggers for dishes 240 mm in diameter (20 pieces). The first firing at 1000°C was performed in a gas kiln, and the second firing after engobing at temperature 1350°C was carried out in a chamber furnace with a pull-out bottom (produced by Ridhammer). No defects were detected after the double firing.

The testing of saggers in multiple firings in the Ridhammer furnace demonstrated their high turnover. The saggers withstood 60 cycles and are still in use.

A microstructural analysis of samples cut out of a sagger after multiple firings indicated an increase in the mullite grain size

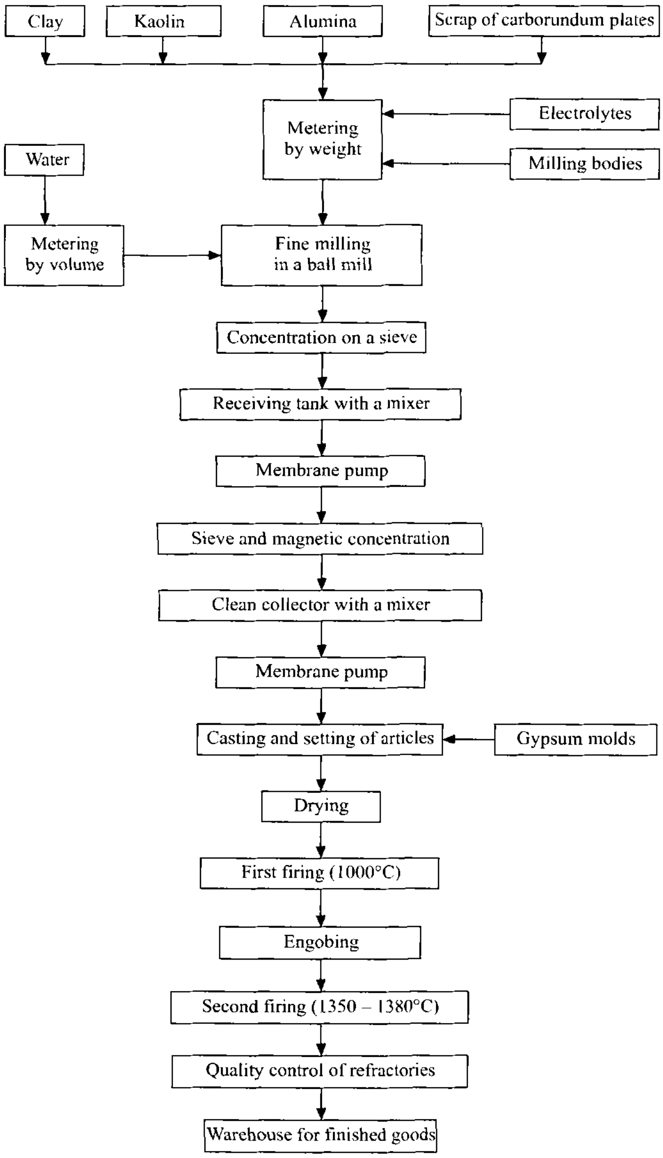

Fig. 2.

from 1 – 5 to 10 – 20 μm, and an increase in the edge width around the silicon carbide grains from 1 to 2 – 4 μm, which corresponds to their fusion. The boundaries of alumina grains become less clear. The porosity changes insignificantly and is within the limits of 19 – 20%, the average size of the pores is 13 μm, and the pore shape is irregular and isometric.

The main economic parameters of comparative production costs of slip and silicon carbide saggers based on pure silicon carbide and based on scrap of silicon carbide plates (data provided by the planning department of the Gzhel' company) are shown in Table 3.

It can be seen that using scrap of silicon carbide plates instead of SiC powder makes it possible to reduce the production cost to approximately one-third. According to the Gzhel' company data, the cost of crushed silicon carbide plate scrap is 310 rubles per ton, whereas the cost of SiC powder, according to the Dulevskii Porcelain Factory data, is 6400 rubles per ton. Thus, the saving in production of saggers based on silicon carbide plate scrap attains 6090 rubles.

The technology of finely disperse heat-resistant refractories was introduced at the Gzhel' company where the process was implemented according to the scheme shown in Fig. 2.

Thus, the use of silicon carbide plate scrap in the production of finely disperse heat-resistant refractories instead of expensive SiC polished powder makes it possible to decrease the production cost of refractories more than 2.5 times, recycle carborundum plate scrap available at industrial enterprises, and free production space involved in storing this waste.

The technology of making finely disperse refractories based on silicon carbide plate scrap is recommended for implementation at factories producing fine ceramic articles.

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